

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C23C 16/00, 16/44, C30B 25/02, 29/22, H01L 39/24, 39/12		A1	(11) International Publication Number: WO 00/15865 (43) International Publication Date: 23 March 2000 (23.03.00)
(21) International Application Number: PCT/FI99/00741		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 13 September 1999 (13.09.99)			
(30) Priority Data: 981959 11 September 1998 (11.09.98) FI			
(71) Applicant (for all designated States except US): ASM MICRO-CHEMISTRY LTD [FI/FI]; Kutojantie 2 B, FIN-02630 Espoo (FI).			
(72) Inventors; and		Published	
(75) Inventors/Applicants (for US only): LESKELÄ, Markku [FI/FI]; Rauduntie 19 D, FIN-02130 Espoo (FI). RITALA, Mikko [FI/FI]; Antreantie 8 B 4, FIN-02140 Espoo (FI). HATANPÄÄ, Timo [FI/FI]; Aamuyöntkuja 3 B, FIN-02210 Espoo (FI). HÄNNINEN, Timo [FI/FI]; Pitkänsillanranta 7 - 9 A 10, FIN-00530 Helsinki (FI). VEHKAMÄKI, Marko [FI/FI]; Rautalammintie 3 B 409, FIN-00550 Helsinki (FI).		With international search report. In English translation (filed in Finnish).	
(74) Agent: SEPO LAINE OY; Itämerenkatu 3 B, FIN-00180 Helsinki (FI).			

(54) Title: METHOD FOR GROWING OXIDE THIN FILMS CONTAINING BARIUM AND STRONTIUM

(57) Abstract

The present invention relates to a method for growing oxide thin films which contain barium and/or strontium. According to the method, such thin films are made by the ALE technique by using as precursors for barium and strontium their cyclopentadienyl compounds. A thin film made by means of the invention has a high permittivity and excellent conformality.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
		KP	Democratic People's				

DK	Denmark	ES	Spain	SI	Slovenia
EE	Estonia	LR	Liberia	SG	Singapore

Method for growing oxide thin films containing barium and strontium

The present invention relates to high permittivity oxide films and superconductive materials which contain barium and/or strontium. A particular object of the invention is the method according to the preamble of Claim 1 for producing such films and materials.

Dielectric thin films having high dielectric constants (permittivities) are required in many sub-areas of microelectronics and optoelectronics. In particular, the continual decrease in the size of microelectronics components has increased the need for the use of such dielectric films. For example, the capacitance of DRAM (Dynamic Random Access Memory) capacitors must remain nearly constant while their size decreases rapidly, and thus it is necessary to replace the previously used SiO_2 and Si_3N_4 with materials which have higher permittivities than these. In optoelectronics, dielectric films having high permittivities can be exploited in, for example, electroluminescence displays, in which the operating voltage of the displays can be reduced by means thereof. Some dielectric materials having high permittivities, e.g. BaTiO_3 , are also ferroelectric materials at normal temperatures, a factor which further extends their potential uses, for example, to NVRAM (Nonvolatile Random Access Memory) and various microelectromechanical applications.

In addition to high permittivities, these dielectric thin films are required to have, among other things, low leakage current densities and high dielectric breakdown fields. The achievement of both of these properties presupposes a dense and flawless film structure. Of course, the properties of the films must be stable in the conditions of use. Furthermore, in particular in microelectronics applications, the conformality of the films, i.e. their capacity to cover surfaces of complicated shapes with a film of a uniform thickness is important, because in the manufacture of microelectronics components it is necessary to deposit films even in deep trenches and holes.

Oxide thin films containing barium and strontium are widely used and researched dielectric

there can be mentioned high-temperature superconductors, e.g. $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$, and dielectric materials lattice- $\text{Bi}_2\text{Sr}_2\text{Ca}_n\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$ and $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$, and dielectric materials lattice-

matched therewith, $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Sr}_2\text{AlTaO}_6$ (D.L. Schulz and T.J. Marks, Advanced Materials 6 (1994) 719). In all of the above-mentioned formulae, n is 1-3 and δ is 0-1. Other oxide films containing barium and strontium include various niobates $(\text{Sr},\text{Ba})\text{Nb}_2\text{O}_6$ and $(\text{Pb},\text{Ba})\text{Nb}_2\text{O}_6$ (L.M. Shepard, Ceramic Bulletin 71 (1992) 85). These films have been 5 manufactured by many different methods, such as the sol-gel method, various physical vapor deposition methods (PVD) (e.g. vaporization, sputtering, laser ablation) and chemical vapor deposition methods (CVD).

Films manufactured by the sol-gel method, by various physical vapor deposition methods 10 (PVD) (e.g. vaporization, sputtering, laser ablation) and by chemical vapor deposition methods (CVD) are of a high quality. Instead, the manufacture of a film of uniform quality and thickness when the surface structure of the piece is complicated will not succeed. Only by the CVD method is it possible to deposit conformal films in deep trenches and holes (S.M. Bilodeau, Solid State Technology, July (1997) 235). Even in the CVD method, high 15 conformality is attained only when the rate of film growth is determined by the rate of the surface reaction and not by the diffusion of the precursors on the film surface. This is achieved when the surface reaction is slower than the diffusion of the precursors on the film surface. The surface reaction is slow at low temperatures, but in such a case the other properties of the film will, however, often remain poor, which is due to both the poor 20 crystallinity of the film and to difficulties in the control of its composition (C.S. Kang et al., Japanese Journal of Applied Physics, Part 1 36 (1997) 6946; M. Kiyotoshi and K. Eguchi, Electrochemical Society Proceedings 97-25 (1997) 1063).

Atomic Layer Epitaxy (ALE), which is also known as Atomic Layer Chemical Vapor 25 Deposition (ALCVD) or Atomic Layer Deposition (ALD), is a known method for the deposition of thin films (US patent publication 4.085.430). In this method, the thin film is deposited by means of alternate saturating surface reactions. These reactions are implemented by feeding gaseous or vaporized precursors into the reactor alternately and by purging the reactor with an inert gas between the precursor pulses (T. Suntola, Thin Solid 30 Films 215 (1992) 84; Niinistö et al., Materials Science and Engineering B 41 (1996) 23). In

The ALE method has previously been used for making TiO_2 films (Ritala et al., Thin Solid Films 225 (1993) 288, Chemistry of Materials 5 (1993) 1174 and 6 (1994) 556), but so far it has not been possible to manufacture the barium- and strontium-containing oxide thin films which are the object of the present invention by the ALE method in a self-controlling manner. Attempts at self-controlling deposition of superconductive films have also failed. The most important reason for not manufacturing the above-mentioned compounds is the lack of suitable precursors for Ba and Sr. Few of the compounds of the said elements are volatile, and so the precursors used in both CVD and ALE have as a rule been of one compound type, i.e. β -diketonates (W.A. Wojtcak et al., Advances in Organometallic Chemistry 40 (1996) 215, Tiitta and Niinistö, Chemical Vapor Deposition 3 (1997) 167). The problem with the β -diketonates of Ba and Sr is that they do not react with the oxygen sources, H_2O , H_2O_2 and O_2 , most typically used in the ALE method, at temperatures at which they would not decompose thermally. Iodides of the said metals have also been used in the CVD method (P. Mårtensson and A. Härsta, Journal of Crystal Growth 156 (1995) 67), but in this case it is necessary to use temperatures which are too high for most applications.

EP application publication No. 344 352 describes a method for making laminated superconductors by an epitaxy method. The ALE method is also mentioned. The application publication also lists suitable organometallic compounds which can be used as precursors in these methods. Barium cyclopentadienyl is also among them. However, in the publication a film has not been deposited by specifically the ALE method and by using specifically barium cyclopentadienyl as the precursor. Furthermore, the EP publication does not provide preferred conditions for the film growth, since it does not state how or in what conditions cyclopentadienyl compounds should be used, how oxygen is introduced into the oxides or what advantages would follow specifically from the use of barium cyclopentadienyl as the precursor in any of the alternative epitaxy methods described in the publication.

It is an object of the present invention to eliminate the deficiencies described above and to

The invention is based on the observation that the barium and strontium compounds

according to the invention are sufficiently stable in a gas phase, and consequently these compounds can be used as precursors in the ALE technique, and thus oxide thin films which contain barium and strontium can be deposited in a controlled manner. The cyclopentadienyl compounds of barium and strontium are such vaporizable compounds. In 5 the deposition of film, the said barium and strontium compounds are used as precursors in a method according to the ALE principle together with a reactive oxygen precursor and a volatile titanium compound.

More specifically, the method according to the invention is characterized by what is stated 10 in the characterizing part of Claim 1.

The invention will be discussed below with the help of the accompanying drawings.

Figure 1 depicts the composition of a multi-component film as a function of the cycle ratio 15 of the various components.

Figure 2 depicts an X-ray diffraction analysis of the thin film.

Figure 3 depicts the permittivities of films deposited at 325 °C, as a function of the cycle 20 ratio, as measured from the structure ITO/SrTiO₃/Al, where ITO is indium-tin oxide.

In the technical solution according to the invention, oxide thin films are deposited in an ALE reactor at a temperature of 100-700 °C, preferably 150-400 °C. Either sheet-form 25 (such as glass or silicon wafer) or pulverous materials can be used as the substrate. According to the ALE method, a cyclopentadienyl compound containing an earth-alkali metal is vaporized, whereafter the reactor is purged with an inert gas, the oxygen precursor is fed into the reactor, and the reactor is purged for a second time with an inert gas. All of these steps together constitute one deposition cycle. The deposition cycle is repeated until the film is of the desired thickness. A multi-component film is obtained by changing the 30 precursor.

strontium are used as precursors by means of the above-mentioned compounds, and correspond to Formulae I-IV.

	M(Cp) ₂	(I)
	M(Cp) ₂ L _n	(II)
	M(Cp)X	(III)
5	M(Cp)XL _n	(IV),

in which formulae

M is Ba or Sr;

10

Cp is a cyclopentadienyl group, the Cp groups present in Formulae I and II being mutually the same or different;

X is a ligand other than Cp, with the valency of -1;

15

L_n is a neutral adduct ligand which binds to a metal by either one or several of its atoms, and n depicts the number of the ligands being bound.

20 In Formulae I-IV the cyclopentadienyl groups may also be in the same molecule. In this case the bridge between two Cp groups is made up of a substituted or unsubstituted C₁-C₆ chain, which may contain a heteroatom which is Si, N, P, Se or S.

Ligand X is preferably β -diketonate or a corresponding sulfur or nitrogen compound, halide, amide, alkoxide, carboxylate or Schiff base.

25

L is preferably

- (i) a hydrocarbon,
- (ii) an oxygen-containing hydrocarbon,
- (iii) a nitrogen-containing hydrocarbon,
- 30 (iv) a sulfur-containing hydrocarbon,

- (vii) a selenium-containing hydrocarbon, and
- (viii) a tellurium-containing hydrocarbon.

Most preferably L is

- (a) an amine or a polyamine,
- (b) a bipyridine,
- 5 (c) a ligand depicted by the formula



10

in which formula G is -O-, -S-, or -NR¹-, where R¹ is hydrogen or a substituted or unsubstituted, cyclic, linear or branched alkyl, alkenyl, aryl, alkylaryl, arylalkyl, alkoxy, thio, cyano or silyl group. The cyclic or aromatic ring of R¹ may contain a heteroatom. The ligand depicted by Formula V may also have either hydrogen or a substituent like R¹ attached to the carbon atoms,

15

- (d) ether or thioether.

The cyclopentadienyl group (Cp) in Formulae I-IV is of the form

20



where m is an integer of 0-5,

25

Cp' is a fused or individual cyclopentadienyl, and

R is a hydrocarbon radical containing 1-20 carbon atoms, preferably a C₅-C₆ hydrocarbon. The R's may be mutually the same or different. R may be a substituted or unsubstituted, cyclic, linear or branched alkyl, alkenyl, aryl, alkylaryl, arylalkyl, alkoxy, thio, amino, cyano or silyl group. The cyclic or aromatic ring of the substituent may contain a heteroatom. Methyl, ethyl, propyl and isopropyl groups can be mentioned as examples of the substituents.

30 Preferably there is used an organometallic complex according to Formula II, where Cp is

which bind to the metal by one atom. Polyamines and polyamides can be mentioned as examples of suitable ligands which bind to the metal by several of their atoms.

According to the invention, the precursor used for the oxide thin film is especially preferably a THF adduct of bis(pentamethylcyclopentadienyl) or bis(triisopropylcyclopentadienyl) of barium or strontium.

5

According to the first preferred embodiment of the invention, the cyclopentadienyl compounds of barium and strontium are used together with a volatile titanium compound (e.g. a halide, alkoxide, cyclopentadienyl, alkylamide) and a reactive oxygen precursor (e.g. H_2O , H_2O_2), in which case $BaTiO_3$, $SrTiO_3$ and $Ba_{1-x}Sr_xTiO_3$ films can be grown by the ALE method at low deposition temperatures (325 °C). The said precursors can also be exploited in ALE deposition of other oxide thin films containing barium and/or strontium.

Below there are listed titanium compounds which have vapor pressures sufficient at a temperature lower than the temperature of the deposition substrate, and which are thus suitable for use in the method according to the present invention. Thus, preferably one or more of the following compounds are used as the volatile titanium compound:

20

- titanium halides, for example $TiCl_4$, $TiCl_3$, $TiBr_3$, TiI_4 , TiI_3 ,
- titanium alkoxides, for example $Ti(OC_2H_5)_4$, $Ti(O^iPr)_4$, $Ti(O^iBu)_4$ and titanium(IV)-ethylhexoxide,
- titanium nitrate ($Ti(NO_3)_4$),
- alkylamino complexes of titanium, for example tetrakis(diethylamino)titanium, tetrakis(dimethylamino)titanium, tetrakis(ethylmethylamino)titanium, tetrakis(isopropylmethylamino)titanium, bis(cyclopentadienyl)bis(dimethylamino)titanium, tris(dimethylamino)(N,N,N'-trimethylethyldiamino)titanium, and tert-butyltris(dimethylamino)titanium; further examples of applicable compounds are described in US patent No. 5,659,057,
- cyclopentadienyl complexes of titanium, for example $Ti(\eta^5-C_5H_5)_2$, $Ti(\eta^5-C_5H_5)(\eta^5-C_5H_5)$, $(\eta^5-C_5H_5)TiR_2$, where R = alkyl (e.g. CH_3), benzyl (C_6H_5) or carbonyl, bis(t-butylcyclopentadienyl)titanium dichloride, bis(pentamethylcyclopentadienyl) titanium dichloride, and $(C_5H_5)_2Ti(CO)_2$,

25

30

35

40

45

50

55

60

65

70

75

80

85

90

95

100

105

110

115

120

125

130

135

140

145

150

155

160

165

170

175

180

185

190

195

200

205

210

215

220

225

230

235

240

245

250

255

260

265

270

275

280

285

290

295

300

305

310

315

320

325

330

335

340

345

350

355

360

365

370

375

380

385

390

395

400

405

410

415

420

425

430

435

440

445

450

455

460

465

470

475

480

485

490

495

500

505

510

515

520

525

530

535

540

545

550

555

560

565

570

575

580

585

590

595

600

605

610

615

620

625

630

635

640

645

650

655

660

665

670

675

680

685

690

695

700

705

710

715

720

725

730

735

740

745

750

755

760

765

770

775

780

785

790

795

800

805

810

815

820

825

830

835

840

845

850

855

860

865

870

875

880

885

890

895

900

905

910

915

920

925

930

935

940

945

950

955

960

965

970

975

980

985

990

995

1000

1005

1010

1015

1020

1025

1030

1035

1040

1045

1050

1055

1060

1065

1070

1075

1080

1085

1090

1095

1100

1105

1110

1115

1120

1125

1130

1135

1140

1145

1150

1155

1160

1165

1170

1175

1180

1185

1190

1195

1200

1205

1210

1215

1220

1225

1230

1235

1240

1245

1250

1255

1260

1265

1270

1275

1280

1285

1290

1295

1300

1305

1310

1315

1320

1325

1330

1335

1340

1345

1350

1355

1360

1365

1370

1375

1380

1385

1390

1395

1400

1405

1410

1415

1420

1425

1430

1435

1440

1445

1450

1455

1460

1465

1470

1475

1480

1485

1490

1495

1500

1505

1510

1515

1520

1525

1530

1535

1540

1545

1550

1555

1560

1565

1570

1575

1580

1585

1590

1595

1600

1605

1610

1615

1620

1625

1630

1635

1640

1645

1650

1655

1660

1665

1670

1675

1680

1685

1690

1695

1700

1705

1710

1715

1720

1725

1730

1735

1740

1745

1750

1755

1760

1765

1770

1775

1780

1785

1790

1795

1800

1805

1810

1815

1820

1825

1830

1835

1840

1845

1850

1855

1860

1865

1870

1875

1880

1885

1890

1895

1900

1905

1910

1915

1920

1925

1930

1935

1940

1945

1950

1955

1960

1965

1970

1975

1980

1985

1990

1995

2000

2005

2010

2015

2020

2025

2030

2035

2040

2045

2050

2055

2060

2065

2070

2075

2080

2085

2090

2095

2100

2105

2110

2115

2120

2125

2130

2135

2140

2145

2150

2155

2160

2165

2170

2175

2180

2185

2190

2195

2200

2205

2210

2215

2220

2225

2230

2235

2240

2245

2250

2255

2260

2265

2270

2275

2280

2285

2290

2295

2300

2305

2310

2315

2320

2325

2330

2335

2340

2345

2350

2355

2360

2365

2370

2375

2380

2385

2390

2395

2400

2405

2410

2415

2420

2425

2430

2435

2440

2445

2450

2455

2460

2465

2470

2475

2480

2485

2490

2495

2500

2505

2510

2515

2520

2525

2530

2535

2540

2545

2550

2555

2560

2565

2570

2575

2580

2585

2590

2595

2600

2605

2610

2615

2620

2625

2630

2635

2640

2645

2650

2655

2660

2665

2670

2675

2680

2685

2690

2695

2700

2705

2710

2715

2720

2725

2730

2735

2740

2745

2750

2755

2760

2765

2770

2775

2780

2785

2790

2795

2800

2805

2810

2815

2820

2825

2830

2835

2840

2845

2850

2855

2860

2865

2870

2875

2880

2885

2890

2895

2900

2905

2910

2915

2920

2925

2930

2935

2940

2945

2950

2955

2960

2965

2970

2975

2980

2985

2990

2995

3000

3005

3010

3015

3020

3025

3030

3035

3040

3045

3050

3055

3060

3065

3070

3075

3080

3085

3090

3095

3100

3105

3110

3115

3120

3125

3130

3135

3140

3145

3150

3155

3160

3165

3170

3175

3180

3185

3190

3195

3200

3205

3210

3215

3220

3225

3230

3235

3240

3245

3250

3255

3260

3265

3270

3275

3280

3285

3290

3295

3300

3305

3310

3315

3320

3325

3330

3335

3340

3345

3350

3355

3360

3365

3370

3375

3380

3385

3390

3395

3400

3405

3410

3415

3420

3425

3430

3435

3440

3445

3450

3455

3460

3465

3470

3475

3480

3485

3490

3495

3500

3505

3510

3515

3520

3525

3530

3535

3540

3545

3550

3555

3560

3565

3570

3575

3580

3585

3590

3595

3600

3605

3610

3615

3620

3625

3630

3635

3640

3645

3650

3655

3660

3665

3670

3675

3680

3685

3690

3695

3700

3705

3710

3715

3720

3725

3730

3735

3740

3745

3750

3755

3760

3765

3770

3775

3780

3785

3790

3795

3800

3805

3810

3815

3820

3825

3830

3835

3840

3845

3850

3855

3860

3865

3870

3875

3880

3885

3890

3895

3900

3905

3910

3915

3920

3925

3930

3935

3940

3945

3950

3955

3960

3965

3970

3975

3980

3985

3990

3995

4000

4005

4010

4015

4020

4025

4030

4035

4040

4045

4050

4055

4060

4065

4070

4075

4080

4085

4090

4095

4100

4105

4110

4115

4120

4125

4130

4135

4140

4145

4150

4155

4160

4165

4170

4175

4180

4185

4190

4195

4200

4205

4210

4215

4220

4225

4230

4235

4240

4245

4250

4255

4260

4265

4270

4275

4280

4285

4290

4295

4300

4305

4310

4315

4320

4325

4330

4335

4340

4345

4350

4355

4360

4365

4370

4375

4380

4385

4390

4395

4400

4405

4410

4415

4420

4425

4430

4435

4440

4445

4450

4455

4460

4465

4470

4475

4480

4485

4490

4495

4500

4505

4510

4515

4520

4525

4530

4535

4540

4545

4550

4555

4560

4565

4570

4575

4580

4585

4590

4595

4600

4605

4610

4615

4620

4625

4630

4635

4640

4645

4650

4655

4660

4665

4670

4675

4680

4685

4690

4695

4700

4705

4710

4715

4720

4725

4730

4735

4740

4745

4750

4755

4760

4765

4770

4775

4780

4785

4790

4795

4800

4805

4810

4815

4820

4825

4830

4835

4840

4845

4850

4855

4860

4865

4870

4875

4880

4885

4890

4895

4900

4905

4910

4915

4920

4925

4930

4935

4940

4945

4950

4955

4960

4965

4970

4975

4980

4985

4990

4995

5000

5005

5010

5015

5020

5025

5030

5035

5040

5045

5050

5055

5060

5065

5070

5075

5080

5085

5090

5095

5100

5105

5110

5115

5120

5125

5130

5135

5140

5145

5150

5155

5160

5165

5170

5175

5180

5185

5190

5195

5200

5205

5210

5215

5220

5225

5230

5235

5240

5245

5250

5255

5260

5265

5270

5275

5280

5285

5290

5295

5300

5305

5310

5315

5320

5325

5330

5335

5340

5345

5350

5355

5360

5365

5370

5375

5380

5385

5390

5395

5400

5405

5410

5415

5420

5425

5430

5435

5440

5445

5450

5455

5460

5465

5470

5475

5480

5485

5490

5495

5500

5505

5510

5515

5520

5525

5530

5535

5540

5545

5550

5555

5560

5565

5570

5575

5580

5585

5590

5595

5600

5605

5610

5615

5620

5625

5630

5635

5640

5645

5650

5655

5660

5665

5670

5675

5680

5685

5690

5695

5700

5705

5710

5715

5720

5725

5730

5735

5740

5745

5750

5755

5760

5765

5770

5775

5780

5785

5790

5795

5800

5805

5810

5815

5820

5825

5830

5835

5840

5845

5850

5855

5860

5865

5870

5875

5880

5885

5890

5895

5900

5905

5910

5915

5920

5925

5930

5935

5940

5945

5950

5955

5960

5965

5970

5975

5980

5985

5990

5995

6000

6005

6010

6015

6020

6025

6030

6035

6040

6045

6050

6055

6060

6065

6070

6075

6080

6085

6090

6095

6100

6105

6110

6115

6120

6125

6130

6135

6140

6145

6150

6155

6160

6165

6170

6175

6180

6185

6190

6195

6200

6205

6210

6215

6220

6225

6230

6235

6240

6245

6250

6255

6260

6265

6270

6275

6280

6285

6290

6295

6300

6305

6310

6315

6320

6325

6330

6335

6340

6345

6350

6355

6360

6365

6370

6375

6380

6385

6390

6395

6400

6405

6410

6415

6420

6425

6430

6435

6440

6445

6450

6455

6460

6465

6470

6475

6480

6485

6490

6495

6500

6505

6510

6515

6520

6525

6530

6535

6540

6545

6550

6555

6560

6565

6570

6575

6580

6585

6590

6595

6600

6605

6610

6615

6620

6625

6630

6635

6640

6645

6650

6655

6660

6665

6670

6675

6680

6685

6690

6695

6700

6705

6710

6715

6720

6725

6730

6735

6740</

heptanedionato)titanium, and tris(2,2,6,6,-tetramethyl-3,5-heptanedionato)-titanium(III).

Especially preferably, titanium tetraisopropoxide ($Ti(O^1C_3H_7)_4$) is used.

5

The oxygen precursor may be any oxygen compound usable in the ALE technique. Preferable oxygen precursors include water, oxygen and hydrogen peroxide, and aqueous solutions of hydrogen peroxide. Ozone (O_3) is an especially preferable oxygen precursor. It is known on the basis of the literature that, if ozone is used as the precursor for oxygen, a 10 denser layer of material is obtained from the forming oxides, and thereby the permittivity of the oxide thin film can be improved.

One or more of the following compounds may also be used as the precursor for oxygen:

- oxides of nitrogen, such as N_2O , NO , and NO_2 ,
- 15 – halide-oxygen compounds, for example chlorine dioxide (ClO_2) and perchloric acid ($HClO_4$), the compatibility of these with earth-alkali metals being, however, limited,
- peracids (-O-O-H), for example perbenzoic acid (C_6H_5COOOH) and peracetic acid (CH_3COOOH),
- 20 – alcohols, such as methanol (CH_3OH) and ethanol (CH_3CH_2OH), and
- various radicals, for example oxygen radical (O^{\cdot}) and hydroxyl radical ($^{\cdot}OH$).

According to a second preferred embodiment, the ratio of the deposition cycles (e.g. $Ti-O$, $Sr-O$ and $Ba-O$) producing the different binary oxides of multicomponent oxide films (e.g. 25 $BaTiO_3$, $SrTiO_3$ and $Ba_{1-x}Sr_xTiO_3$) is controlled. If, for example, Sr/Ti is 0.8-1.2, preferably approx. 1, a crystalline film is obtained (cf. Example 1). Thus the composition can be controlled simply and with precision. In order that the composition of the film should be uniform, the deposition cycles are carried out so that the different materials become mixed as completely as possible, i.e. there will be 1-10, preferably 1-2 similar cycles in 30 succession.

becomes crystalline during postannealing. The postannealing is carried out at a temperature higher than the growth temperature, and its duration may vary. According to a preferred embodiment of the invention, the duration of the postannealing is 60 min, and it is carried out in an air stream at 500 °C.

5

Considerable advantages are gained with the help of the invention. Since according to the ALE method the film grows through saturating surface reactions, the growth is self-controlling, which in turn ensures excellent conformality. As is evident from the above, cyclopentadienyl compounds of strontium and barium can be used as vaporizing 10 components within a wide temperature range, in which case the structure of the thin film made and its crystallinity can be effectively controlled by the selection of the reaction temperature and the metal mixing ratio and by a potential post-treatment. The present precursors are especially advantageous for use in the ALE technique also for the reason that they will not leave significant carbon or hydrogen residues in the final product. On the 15 other hand, the dielectric constants of oxide thin films containing barium and strontium are very high, and thus the oxides of specifically barium and strontium are especially suitable as materials for dielectric thin films. Owing to their high dielectric constants they are especially suitable for memory circuits and for gate oxides. By the use of cyclopentadienyl compounds of barium together with a volatile titanium compound, a low-temperature 20 growth process is achieved, which is important in most applications of dielectric films.

In the context of the present invention, by dielectric oxide thin film is meant a thin film having a high permittivity. The permittivity varies according to the thickness of the film so that the permittivity of a thinner film is lower. It can be noted as an example that for a film 25 approx. 50 nm thick a high permittivity is approx. 50 or more, preferably approx. 100 or more.

Thin films according to the invention are preferably used as dielectric films of various electronics components. Films according to the invention are deposited, for example, on 30 platinum (Pt), RuO₂, IrO₂, SrRuO₃, LaSrCoO₃, IrO₂/Ir, RuO₂/Pt, silica (SiO₂), silicon nitride and silicon surfaces

for example $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (x is 0-1), $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$ and $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$, and dielectric materials lattice-matched therewith, such as $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$, and $\text{Sr}_2\text{AlTaO}_6$ (D. L. Schulz and T. J. Marks, Advanced Materials 6 (1994) 719).

5 Three examples are presented below in order to illustrate the invention.

Example 1

10 SrTiO₃ films were grown in a flow-type F-120 ALE reactor (Mikrokemia Oy) at a temperature of 325 °C. The strontium precursor used was the THF adduct of bis(triisopropylcyclopentadienyl) strontium, $\text{Sr}(\text{C}_5(\text{C}_3\text{H}_7)_3\text{H}_2)\text{THFG}_p$, in which $p = 0-2$ and THF is tetrahydrofuran, and which was vaporized in the reactor by heating it to a temperature of 100 °C. The titanium precursor used was titanium tetraisopropoxide (Ti(O'C₃H₇)₄), which was vaporized in the reactor at a temperature of 40 °C. The oxygen source used was water, which was fed into the reactor from outside it. The growth of TiO₂ from the said precursors has been described previously (Ritala et al., Chemistry of Materials 5 (1993) 1174).

15 The growth of SrTiO₃ was implemented by using alternate Ti-O and Sr-O deposition cycles. The Ti-O cycle was made up of four steps: (i) an 0.6 s pulse of Ti(O'C₃H₇)₄, an 0.5 s purge with inert nitrogen gas, (iii) an 0.6 pulse of H₂O, and (iv) an 0.5 s purge with nitrogen gas. Respectively, the composition of the Sr-O cycle was: (i) an 0.6 s pulse of $\text{Sr}(\text{C}_5(\text{C}_3\text{H}_7)_3\text{H}_2)\text{HTF}_p$, (ii) an 0.5 s purge with nitrogen gas, (iii) an 0.5 s pulse of H₂O, and (iv) an 0.5 s purge with nitrogen gas. The composition of the film was controlled by the ratio of the Ti-O and Sr-O cycles. The alternation of the Ti-O and Sr-O cycles was implemented so that there were at maximum two similar cycles in succession. For example, the cycle ratio Ti-O/Sr-O = 1:1 was achieved by repeating the cycling formula q[(Ti-O)(Sr-O)] and the ratio Ti-O/Sr-O = 3:4 by means of the formula q[(Ti-O)(Sr-O)(Ti-O)(Sr-O)(Ti-O)(Sr-O)], in which formulae q indicates how many times the said cycling was repeated.

20

25

30

When the values were plotted against the number of cycles, the following results were obtained according to the cycle ratio (Figure 1). The linearity of the curve shown in the figure is an indication

that the composition can well be controlled by means of the cycle ratio. Films having Sr/Ti ratios close to 1 were, according to an X-ray diffraction analysis, crystalline SrTiO₃ (Figure 2). TOF-ERDA (Time-of-Flight Elastic Recoil and Detection Analysis) showed that the films contained carbon and hydrogen residues lower than 0.2 at.%, the other possible impurity residues being so low that they cannot be detected by the method concerned.

Figure 3 shows the effect of the post-treatment on the permittivity of the film. The permittivities of films without post-treatment are at maximum 118, but annealing in air at a temperature of 500 °C for 60 min increases permittivity significantly, the highest values being 180. The postannealing also increased the intensity of X-ray reflections, showing an improved film crystallinity.

Example 2

15

The process according to Example 1 was repeated using a growth temperature of 250 °C. The films thus grown were amorphous, but they crystallized when they were heated in air at 500 °C for 60 min.

20

Example 3

BaTiO₃ films were grown in the manner described in Example 1, but by using instead of Sr(C₅(C₃H₇)₃H₂)₂THF_p a THF adduct of bis(pentamethylcyclopentadienyl)barium, 25 Ba(C₅(CH₃)₄)THF_p, where x = 0.2. The deposition temperature was 250 °C. When a deposition cycle ratio of (Ti-O)/(Ba-O) = 6:5 was used, an amorphous film was obtained. When this film was heated in air at 500 °C for 60 min, it crystallized as BaTiO₃, for which a measurement showed a permittivity of 165.

Claims:

1. A method for growing oxide thin films, characterized in that the films are produced by the ALE process by using as the precursor cyclopentadienyl compounds of strontium and/or barium, together with one or more volatile titanium compounds and a reactive oxygen precursor.
5
2. The method according to Claim 1, characterized in that the oxide thin film to be grown is dielectric.
10
3. The method according to Claim 1 or 2, characterized in that there are 1-10, preferably 1-2, similar growth cycles in succession, one growth cycle being made up of the feeding of a Ba compound, Sr compound or volatile titanium compound; an inert purge; the feeding of a precursor for oxygen; and a second inert purge.
15
4. The method according to any of Claims 1 - 3, characterized in that the cycle ratio of the alkaline earth metal compound and the titanium compound is 0.8-1.2.
5. The method according to any of Claims 1 - 4, characterized in that the volatile titanium compound is a titanium halide, titanium alkoxide, titanium nitrate ($Ti(NO_3)_4$), an alkylamino complex of titanium, a cyclopentadienyl complex of titanium, a silylamido complex of titanium, titanium dialkyldithiocarbamate, or titanium- β -diketonate.
20
6. The method according to any of the preceding claims, characterized in that the film growth substrate is a platinum (Pt), RuO_2 , IrO_2 , $SrRuO_3$, $LaSrCoO_3$, IrO_2/Ir , RuO_2/Pt , silica (SiO_2), silicon nitride or silicon surface.
25
7. The method according to any of the preceding claims, characterized in that the reactive oxygen precursor used is oxygen (O_2), water vapor, hydrogen peroxide or an aqueous solution of hydrogen peroxide, and/or ozone.
30

11. The precursor is a salt of a metal, which

- M is Sr or Ba,

- Cp is a fused or single cyclopentadienyl group of the form $Cp'R_mH_{5-m}$, where
 - m is an integer 0-5 and
 - R is a hydrocarbon group, the hydrocarbon groups being mutually either the same or different,
- 5 - the Cp groups are either the same or different,
- L_n is a neutral adduct ligand which binds to the metal by one or several of its atoms.

9. The method according to any of Claims 1 - 7, characterized in that

10

- the precursor for Sr and/or Ba is of the form $M(Cp)X$ or $M(Cp)XL_n$, where
- M is Sr or Ba,
- Cp is a fused or single cyclopentadienyl group $Cp'R_mH_{5-m}$, where
 - m is an integer 0-5 and
 - R is a hydrocarbon group, the R's being mutually either the same or different,
- X is a ligand, other than Cp, having a valence of -1 and
- L is a neutral adduct ligand which binds to the metal by one or several of its atoms.

20

10. The method according to Claim 8 or 9, characterized in that the cyclopentadienyl group is cyclopentadienyl, pentamethylcyclopentadienyl, triisopropylcyclopentadienyl, indenyl, or fluorenyl.

25

11. The method according to Claim 8 or 9, characterized in that the Cp groups are contained in the same molecule.

12. The method according to Claim 11, characterized in that the bridge between two Cp groups is made up of a substituted or unsubstituted $C_1 - C_6$ carbon chain.

30

13. The method according to Claim 12, characterized in that the carbon chain

14. The method according to Claim 8 or 9, characterized in that R is a substituted or unsubstituted, cyclic, linear or branched alkyl, alkenyl, aryl, alkylaryl, arylalkyl, alkoxy, thio, amino, cyano or silyl group.

5 15. The method according to Claim 8 or 9, characterized in that the neutral adduct ligand L is

(i) a hydrocarbon,
 (ii) an oxygen-containing hydrocarbon,
 (iii) a nitrogen-containing hydrocarbon,
 10 (iv) a sulfur-containing hydrocarbon,
 (v) a phosphorus-containing hydrocarbon,
 (vi) an arsenic-containing hydrocarbon,
 (vii) a selenium-containing hydrocarbon, and/or
 (viii) a tellurium-containing hydrocarbon.

15 16. The method according to Claim 8 or 9, characterized in that L is

(a) an amine or polyamine,
 (b) a bipyridine,
 (c) a ligand depicted by the formula

20  (V)

25 in which formula G is -O-, -S-, or -NR¹-, where R¹ is hydrogen or a substituted or unsubstituted, cyclic, linear or branched, alkyl, alkenyl, aryl, alkylaryl, arylalkyl, alkoxy, thio, cyano or silyl group, and in each carbon atom of the ring according to the formula there is an R¹-like substituent, which are either mutually the same or different,

30 (d) ether, or

18. The method according to Claim 9, characterized in that X is a β -ketonate or a corresponding sulfur or nitrogen compound, alkyl, halide, amide, alkoxide, carboxylate or Schiff base.

5

19. The method according to any of the preceding claims, characterized in that the growth of the film takes place at 250-300 °C, and the postannealing carried out after the growth takes place at a temperature higher than the deposition temperature, preferably at 500 °C.

1/3

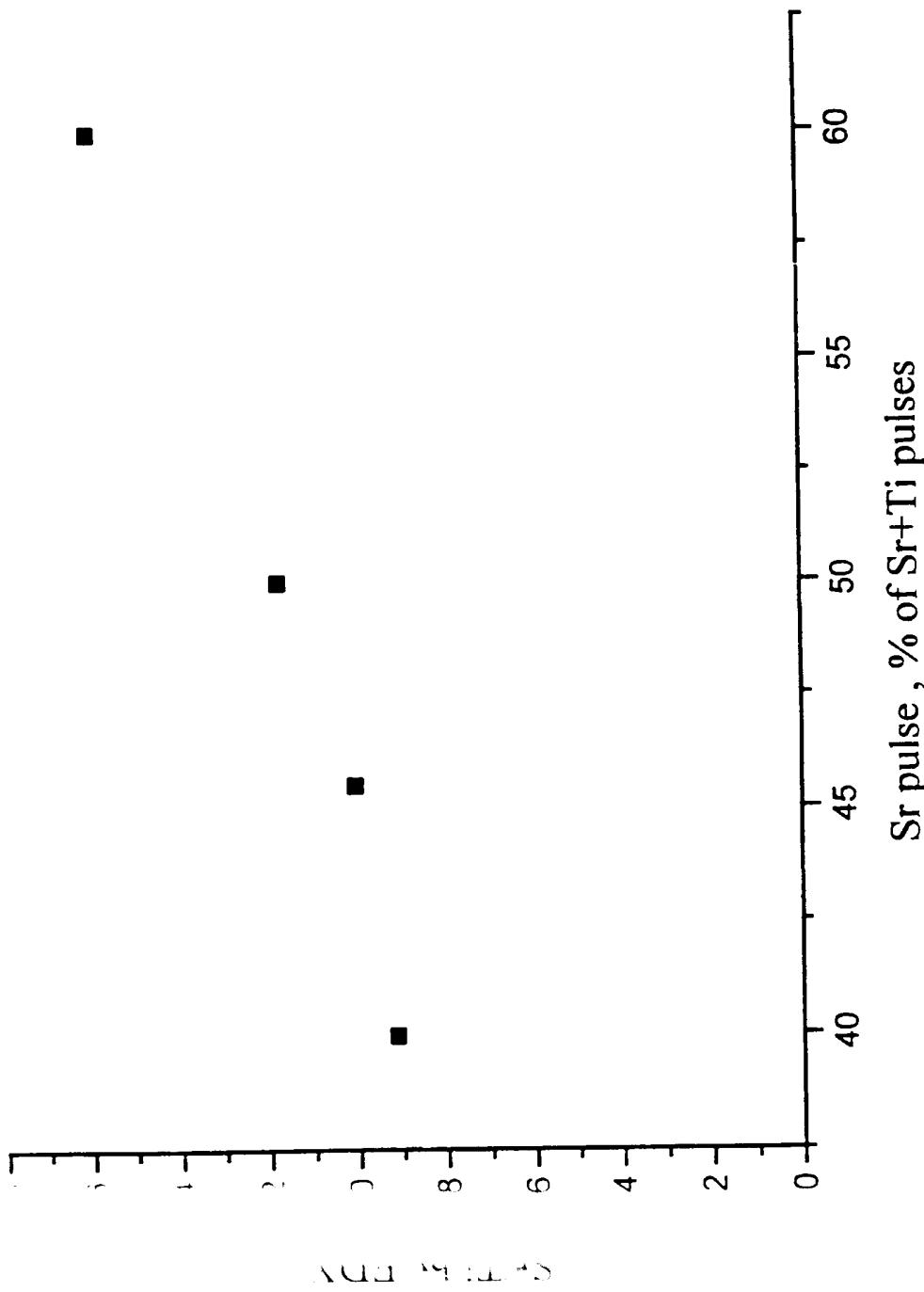
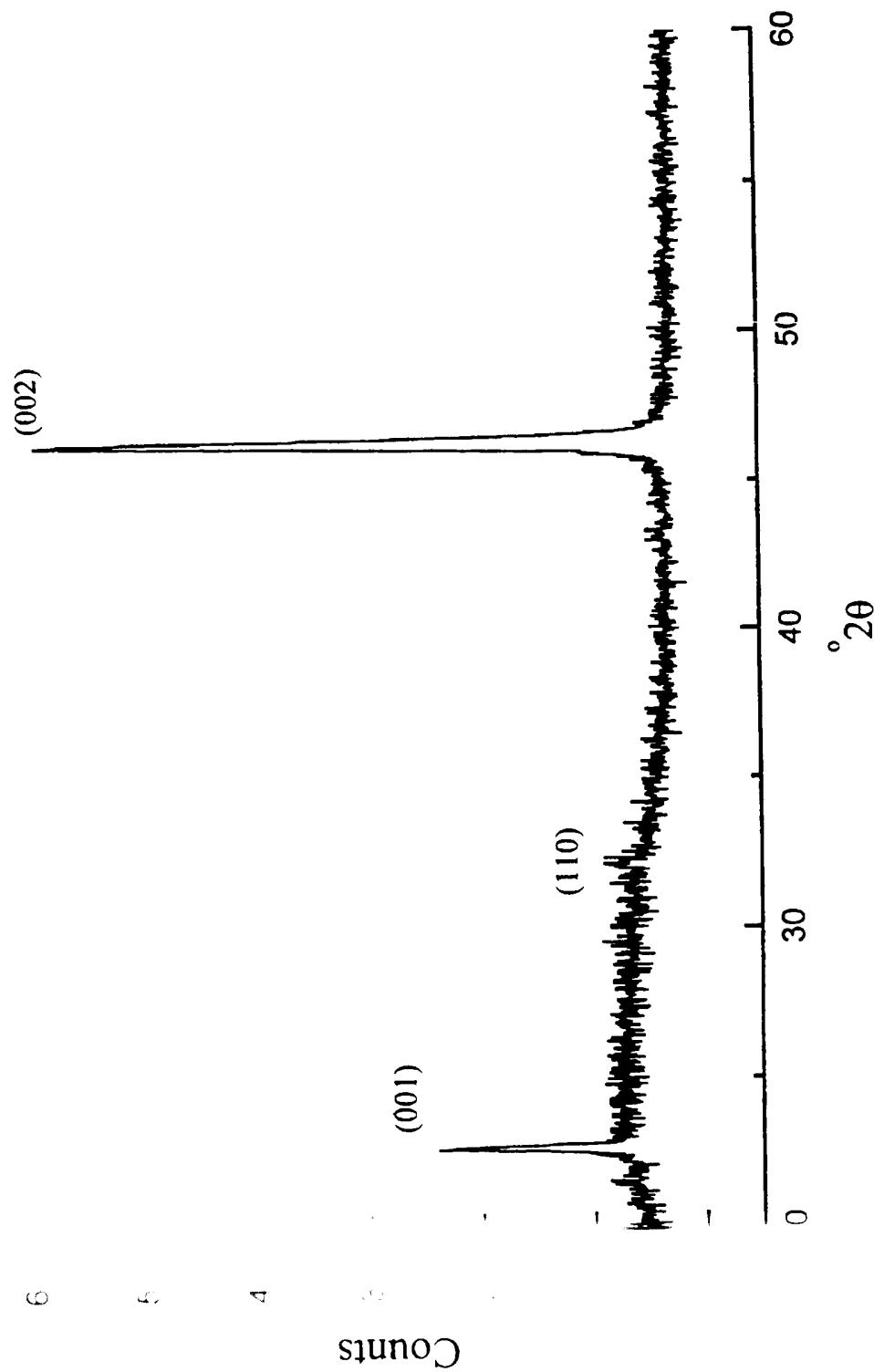


Fig. 1

2/3

**Fig. 2**

3/3

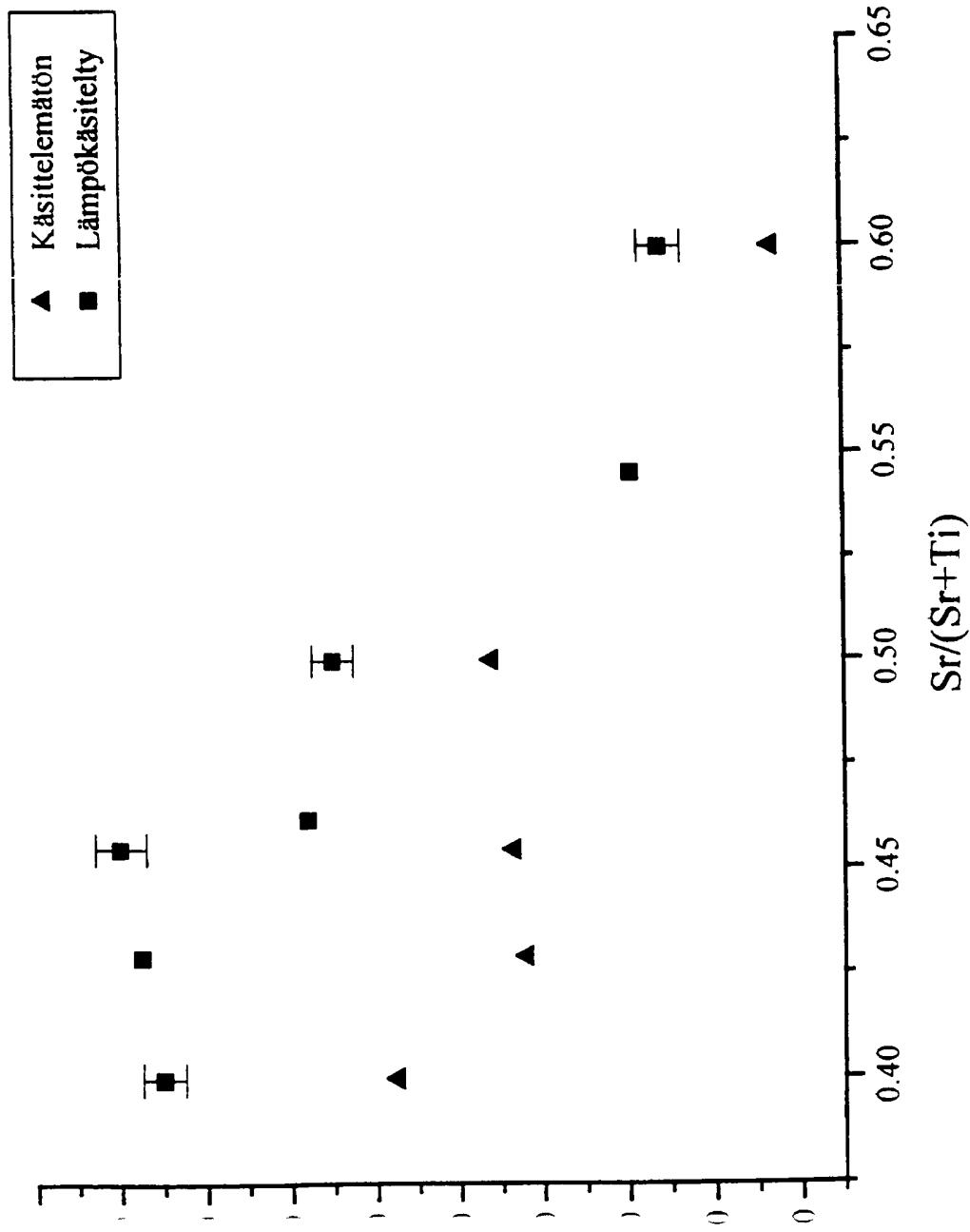


Fig. 3

1
INTERNATIONAL SEARCH REPORTInternational application No.
PCT/FI 99/00741

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C23C 16/00, C23C 16/44, C30B 25/02, C30B 29/22, H01L 39/24, H01L 39/12
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C23C, C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0344352 A1 (INTERNATIONAL BUSINESS MACHINES CORPORATION), 6 December 1989 (06.12.89), page 3, line 46 - page 4, line 15; page 5, line 8 - line 20; page 6, line 2 - line 11, abstract --	1-19
X	US 4927670 A (AHMET ERBIL), 22 May 1990 (22.05.90), column 2, line 58 - line 59; column 3, line 65 - column 4, line 11; column 5, line 18 - line 22, column 8, line 35 - line 49; column 11, line 31 - line 33, abstract --	1-19
X	FR 2626110 A1 (THOMSON CSF), 21 July 1989 (21.07.89), page 5, line 11 - line 23; page 6, line 1 - line 30, figure 2 --	1-19

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

2 December 1999

14-12-1999

Name and mailing address of the ISA
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. + 46 8 666 02 86

Authorized officer

Ulrika Nilsson/ELY
Telephone No. + 46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 99/00741

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4058430 A (TUOMO SUNTOLA ET AL), 15 November 1977 (15.11.77), abstract	1-19
A	Materials Science and Engineering, Volume B41, 1996, Lauri Niinistö et al, "Synthesis of oxide thin films and overlayers by atomic layer epitaxy for advanced applications", page 23 - page 29, page 27, column 2, line 44 - page 28, column 1, line 17	19

INTERNATIONAL SEARCH REPORT

Information on patent family members

02/11/99

International application No.

PCT/FI 99/00741

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0344352 A1	06/12/89	SE 0344352 T3		
		AT 112418 T		15/10/94
		CA 1330193 A		14/06/94
		DE 3851701 D, T		30/03/95
		JP 7061920 B		05/07/95
		US 5439876 A		08/08/95
US 4927670 A	22/05/90	NONE		
FR 2626110 A1	21/07/89	NONE		
US 4058430 A	15/11/77	AT 381122 B		25/08/86
		AT 868675 A		15/01/86
		AU 505960 B		06/12/79
		AU 8666275 A		26/05/77
		BE 835906 A		16/03/76
		BR 7507724 A		10/08/76
		CA 1066174 A		13/11/79
		CH 618469 A		31/07/80
		CS 249502 B		12/03/87
		DD 122479 A		12/10/76
		DE 2553048 A,B,C		10/06/76
		DK 152060 B,C		25/01/88
		DK 539875 A		30/05/76
		FI 52359 B,C		02/05/77
		FI 347374 A		30/05/76
		FR 2292517 A,B		25/06/76
		GB 1495987 A		21/12/77
		HK 64880 A		21/11/80
		IN 143912 A		05/02/78
		JP 1147355 C		26/05/83
		JP 51077589 A		05/07/76
		JP 57035158 B		27/07/82
		NL 173824 B,C		17/10/83
		NL 7513284 A		01/06/76
		SE 393967 B,C		31/05/77
		SE 401986 B,C		12/06/78
		SE 7513336 A		31/05/76
		ZA 7507128 A		27/10/76